

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C23C 24/08, 10/30, 30/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/66102</b> <b>(43) International Publication Date:</b> 23 December 1999 (23.12.99)
<b>(21) International Application Number:</b> PCT/FI99/00519 <b>(22) International Filing Date:</b> 14 June 1999 (14.06.99) <b>(30) Priority Data:</b> 981357 12 June 1998 (12.06.98) FI <b>(71) Applicant (for all designated States except US):</b> VALTION TEKNILLINEN TUTKIMUSKESKUS [FI/FI]; Vuorim- iehentie 5, FIN-02150 Espoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KOSKINEN, Jari [FI/FI]; Valtion teknillinen tutkimuskeskus, Metallimiehenkuja 2-4, FIN-02150 Espoo (FI). HAIMI, Eero [FI/FI]; Val- tion teknillinen tutkimuskeskus, Metallimiehenkuja 2-4, FIN-02150 Espoo (FI). <b>(74) Agent:</b> PAPULA REIN LAHTELA OY; Fredikinkatu 61 A, P.O. Box 981, FIN-00101 Helsinki (FI).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> <i>In English translation (filed in Finnish).</i>
<b>(54) Title:</b> METHOD FOR FORMING A NICKEL-TITAN PLATING  <b>(57) Abstract</b>  Method for forming a nickel-titan plating, in which method a plating material mainly consisting of nickel-titan is hot pressed onto the surface to be plated.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## METHOD FOR FORMING A NICKEL-TITAN PLATING

The present invention relates to a method for forming a nickel-titan plating.

Nickel-titan (NiTi) is an intermetallic compound. A form of this compound having a certain microstructure is known to have pseudoelastic properties. In this context, pseudoelasticity refers to an unusually large reversible expansion after stress, a phenomenon not based on the ordinary elasticity of materials that is associated with the stretching of atomic bonds. Due to its pseudoelasticity, NiTi may have a maximum reversible expansion as large as 8%, depending on the exact composition, microstructure and temperature of the compound. Typically, it has been established that, due to pseudoelasticity, NiTi compounds have an excellent cavitation strength, and they have also been found to have a good erosion and corrosion resistance in different environments. In particular, NiTi has proved to have a very good resistance to particle, liquid droplet and cavitation erosion. These properties make NiTi compounds an ideal material for use in e.g. water turbine blades and in process industry equipment, such as pumps, mixers, etc.

As NiTi compounds are expensive and difficult to manufacture, it is not economical to make whole parts from NiTi. Instead, in many cases the same advantages and properties can be obtained by plating the desired object with NiTi.

However, NiTi is a difficult plating material because the NiTi microstructure important for pseudoelasticity easily gets destroyed.

As to plating methods, deposition welding and hot spraying involve the problems that it is difficult to achieve a sufficient adhesion at the junction surface and that the microstructure and therefore the properties, especially pseudoelasticity, are difficult to control. For these reasons, the plating methods re-

ferred to are not practical where different surfaces and objects are to be protected with a NiTi plating.

A NiTi plating can also be formed by an explosive plating method, which has yielded better results. The method in question is presented in specification US 5,531,369.

Due to the nature of explosive plating, the area to be plated cannot be of a very complex nature in respect of geometry, which is a significant limitation regarding the shape of objects to be plated and therefore the range of use of NiTi plated objects. In the case of large surfaces to be plated, the size of the explosive charge to be used constitutes a limitation.

The object of the invention is to eliminate the problems referred to above. A specific object of the invention is to develop a relatively simple NiTi plating method which can be used to form a plating on geometrically complex and even large surfaces and which produces a plating possessing pseudoelastic properties.

The features characteristic of the invention are presented in the claims.

In the method of the invention, a plating is produced by hot-pressing plating material onto the surface of the object to be plated. The method is implemented using e.g. axial, isostatic or some other known type of hot pressing.

Hot pressing is accomplished using a pressing element and a heating element. The pressing element is arranged to press the plating material against the surface of the object to be plated and the heating element is arranged to heat the area to be pressed. The action of the pressing element may be e.g. hydraulic, mechanical or some other known type of action. The action of the heating element may be any known type of heating action.

The pressure and temperature used in the hot pressing operation are so selected that the surface to be plated and the plating material are in a solid state in the hot pressing conditions. A solid state is conducive to the formation of the desired boundary layer structure and to the formation of the micro-structure of the plating.

The pressure, temperature and pressing time used in the hot pressing operation all have an effect on the pseudoelasticity and tensions of the plating produced and also on the thickness and nature of the reaction layer that may be formed during the pressing. In addition, these properties can be influenced by varying the material of the surface to be plated and the granular size and amount of e.g. a powdery plating material.

The pressure and temperature to be used in the hot pressing operation are preferably so selected that substantially no tensions due to different thermal expansion coefficients are produced between the object to be plated and the plating material even when the plated object cools down. Such tensions impair the adhesion of the plating and have an adverse effect on the plating structure.

The pressure and temperature used in the hot pressing operation are preferably so high that the plating material forms a continuous plating on the surface of the object to be plated.

The pressure used in the hot pressing operation is preferably in the range of 70-150 MPa, more preferably 90-120 MPa.

The temperature used in the hot pressing operation is preferably in the range of 700-1400°C, more preferably 800-1200°C.

The plating material and the surface of the object to be plated are preferably hot-pressed against

each other for over 1.5 hours, more preferably over 2 hours, e.g. about 3 hours.

At the final stage of the hot pressing operation, the surface is allowed to cool down, or it is cooled down. The cooling rate is preferably below 5°C/min, e.g. 4.6°C/min, and pressing is continued during the cooling phase. A low cooling rate promotes the formation of the microstructure and prevents tensions due to differences between the thermal expansion coefficients.

The plating material preferably has a nickel content of about 48-57 atom percent in relation to the total amount of nickel and titan. The plating material may also contain small amounts of other materials. The plating material may be in the form of wire, powder or sheet.

The surface to be plated is preferably of such material that the reaction layer formed during hot pressing at the boundary layer between the plating material and the surface to be plated will bind the plating to the surface to be plated.

The surface to be plated is preferably made of austenitic steel. When NiTi is hot-pressed onto the surface of austenitic steel at correct temperature and pressure, a reaction layer is formed at the boundary layer between steel and NiTi that binds the plating to the steel surface extremely well.

By the method of the invention, various objects can be easily NiTi-plated so that the plating shows a microstructure and properties characteristic of the pseudoelasticity of NiTi. When objects are plated by the method of the invention, a reaction layer allowing excellent plating adhesion can be created at the boundary layer between the object to be plated and the plating material. The invention allows large and geometrically more complex surfaces than before to be plated relatively economically, thus making

it possible to use NiTi plated parts on a much larger scale than before and in new areas of technology. In the method of the invention, the thickness and granular structure of the plating can be varied in more diversified ways than before.

In the following, the invention will be described by the aid of an example embodiment.

In a preferred embodiment of the invention, powdery NiTi compound is hot pressed onto the surface of AISI 316 type austenitic steel at a temperature of about 900°C and at a pressure of about 100MPa for about 3 hours, whereby the NiTi compound is compacted as a pseudoelastic plating on the steel surface and a tough metastable titan-enriched reaction layer is formed at the boundary layer between the steel and the NiTi compound. The plated object is allowed to cool down at a rate below 5°C/min, about 4.6°C/min, while pressing is continued during the cooling phase.

The object to be plated is a ship's propeller, a water turbine blade, a pump for process industry, a valve, a mixer or some other corresponding device.

The above example has been presented in order to illustrate the invention, without limiting it in any way.

## CLAIMS

1. Method for forming a nickel-titan plating, characterized in that, in the method, a plating material mainly consisting of nickel-titan is  
5 hot pressed onto the surface to be plated.

2. Method as defined in claim 1, characterized in that the hot pressing is performed axially.

3. Method as defined in claim 1, characterized in that the hot pressing is performed  
10 isostatically.

4. Method as defined in claim 1, 2 or 3, characterized in that a pressing device and a heating device are used, of which the heating device  
15 is used to heat the plating material and the pressing device is used to press the plating material and the surface to be plated against each other.

5. Method as defined in any one of the preceding claims 1 - 4, characterized in that  
20 the pressure and temperature used in the hot pressing operation are so selected that the surface to be plated and the plating material remain in solid state.

6. Method as defined in any one of the preceding claims 1 - 5, characterized in that  
25 the pressure and temperature used in the hot pressing operation are so selected that substantially no tensions due to differences regarding thermal expansion coefficients are produced between the surface to be plated and the plating material.

7. Method as defined in any one of the preceding claims 1 - 6, characterized in that  
30 the pressure and temperature used in the hot pressing operation are so selected that the plating material forms a compact plating on the surface to be plated.

8. Method as defined in any one of the preceding claims 1 - 7, characterized in that  
35



the pressure used in the hot pressing operation is 70-150MPa, preferably 90-120MPa.

9. Method as defined in any one of the preceding claims 1 - 8, characterized in that  
5 the temperature used in the hot pressing operation is 700-1400°C, preferably 800-1200°C.

10. Method as defined in any one of the preceding claims 1 - 9, characterized in that  
10 the plating material and the surface to be plated are hot-pressed against each other for over 1.5 hours, preferably over 2 hours, most preferably about 3 hours.

11. Method as defined in any one of the preceding claims 1 - 10, characterized in that  
15 the surface is cooled down as a continuation of the hot pressing operation.

12. Method as defined in claim 11, characterized in that during the cooling phase the temperature is reduced at a rate below 5°C/min.

20 13. Method as defined in claim 11 or 12, characterized in that the pressing is continued while the surface is being cooled down.

14. Method as defined in any one of the preceding claims 1 - 13, characterized in that  
25 the plating material contains 48-57 atom percent nickel in relation to the total amount of nickel and titan.

15. Method as defined in any one of the preceding claims 1 - 14, characterized in that  
30 the plating material is in a powdery, sheet-like or wire-like form.

16. Method as defined in any one of the preceding claims 1 - 15, characterized in that  
35 the surface to be plated is of such material that a strong metastable boundary layer is formed during hot pressing between the plating material and the surface to be plated.

17. Method as defined in any one of the preceding claims 1 - 16, characterized in that at least part of the surface to be plated is made of austenitic stainless steel.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00519

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 24/08, C23C 10/30, C23C 30/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C, B22F, B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 1621392 A (HENRY WIGGIN & CO. LTD), 6 May 1971 (06.05.71), claims 1,8	1-2,4-9,11, 14-17
A	--	3,10,12-13
A	US 4252867 A (KEIJI NEMOTO ET AL), 24 February 1981 (24.02.81), abstract	1-17
	-- -----	

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 October 1999

Date of mailing of the international search report

15-10-1999

Name and mailing address of the ISA/

Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Marianne Bratsberg/MP  
Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

28/09/99

International application No.

PCT/FI 99/00519

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1621392 A	06/05/71	BE 703699 A SE 340742 B	11/03/68 29/11/71
US 4252867 A	24/02/81	JP 54102050 A	11/08/79